(19) World Intellectual Property Organization

International Bureau





(43) International Publication Date 23 December 2004 (23.12.2004)

PCT

(10) International Publication Number WO 2004/111336 A1

(51) International Patent Classification⁷: 19/56, 21/16, 27/06 // 17/36, 17/37

D21H 17/34,

(21) International Application Number:

PCT/FI2004/000329

(22) International Filing Date: 31 May 2004 (31.05.2004)

(25) Filing Language:

Finnish

(26) Publication Language:

English

(30) Priority Data:

20030905

17 June 2003 (17.06.2003) F

(71) Applicant (for all designated States except US): UPM-KYMMENE CORPORATION [FI/FI]; Eteläesplanadi 2, FI-00130 Helsinki (FI).

(72) Inventors; and

(75) Inventors/Applicants (for US only): KOSKINEN, Kaj [FI/FI]; Eerolankaari 8, FI-37630 Valkeakoski (FI). RIS-SANEN, Mikko [FI/FI]; Rengastie 24 A 5, FI-37630 Valkeakoski (FI).

(74) Agent: GUSTAFSSON, Helmer; P.O. Box 40, FI-37601 Valkeakoski (FI).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

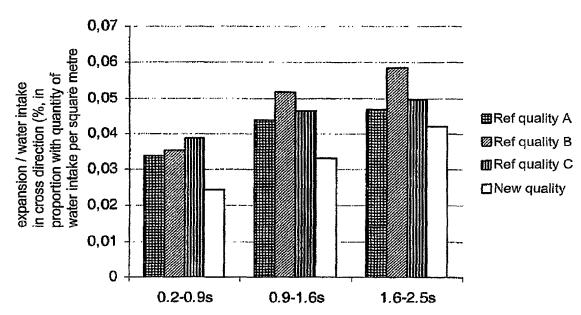
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SURFACE SIZED PAPER



(57) Abstract: The invention relates to a paper comprising a base paper and, on at least one side of the base paper, a surface size layer comprising an inorganic pigment and a polyvinyl alcohol (PVA). The surface size layer comprises an acrylic alkylene copolymer.

1

Surface sized paper

5

10

15

20

25

30

35

The present invention relates to a paper comprising a base paper and, on at least one side of the base paper, a surface size layer comprising inorganic pigment and polyvinyl alcohol (PVA).

The surface sizing of a glazing-type base paper with a surface sizing agent comprising an inorganic filler and polyvinyl alcohol, is known from prior art. The polyvinyl alcohol is a good film forming agent and is therefore commonly used in surface sizing agents. However, the properties of the surface sizing agents include deficiencies which must be compensated for by, for example, strong calendering treatments, to make the surface of the base paper as free from pores as possible before its siliconization. Furthermore, the surface sizing agents must be compatible with silicon in such a way that the silicon can adhere to and reticulate on the surface sizing agent.

The paper according to the invention is characterized in that the surface sizing layer comprises an acrylic alkylene copolymer and/or its derivatives.

When the surface sizing layer of the paper according to the invention comprises an acrylic alkylene copolymer and/or its derivatives, the surface energy of the surface sized paper can be adjusted to such a level that the siliconizability is improved. The improvement in the siliconizability means, among other things, lower silicon consumption, better results in Shirlastain colour tests, and lower release values of the siliconized paper. The addition of an acrylic alkylene copolymer to the surface sizing agent makes the surface of the surface-sized paper more hydrophobic, wherein the surface of the paper does not necessarily need to be treated to be completely poreless by calendering treatments.

The base paper used for the paper according to the invention can be a glazing-type paper or a kraft paper.

2

The glazing paper refers to a paper which is made of chemical pulp and whose grammage is typically from 50 to 150 g/m². Good transparency is typically required of the glazing paper; for a 60 g/m² paper, it is typically at least 45, measured with visible light (ISO 2469:1994). Because glazing paper is used as the base paper for release paper, a poreless surface is a requirement for good siliconizability. The poreless surface can be achieved with calendering treatments and surface sizing. The paper can be either calendered first and then surface sized, or surface sized first and then calendered. Preferably, the calendering is performed first, wherein a calender with more than one nip is preferably used in the calendering. The calender can be a multi-nip calender or a supercalender. In the calender, at least one nip is formed between a hard-faced roll and a soft counter surface. To produce glazing paper, the moisture content of the paper is preferably at least 14 wt-% before the calendering. Now that the surface sizing agent according to the invention is used, however, the calendering treatment is not as critical as before, because the hydrophobic property of the surface sizing agent can be used to compensate for the porosity left after the calendering treatment.

20

25

30

5

10

15

The surface sizing agent according to the invention comprises at least an inorganic pigment and an adhesive. The adhesive comprises a polyvinyl alcohol and an acrylic alkylene copolymer, such as an acrylic ethylene copolymer, and/or its derivatives. The acrylic alkylene copolymer and/or its derivatives mean that the acrylic alkylene copolymer is mixed, before mixing with the surface sizing agent, with an aqueous solution of a strong base, such as sodium hydroxide, and in this way a water-soluble salt is obtained from the acrylic alkylene copolymer. That is, the acrylic alkylene copolymer is first added into the solution, and by the effect of the base, it is converted at least partly to the form of a water-soluble salt. The content of the acrylic alkylene copolymer is normally from 15 to 25 wt-% of the solution comprising water, a suitable base and said acrylic alkylene copolymer. The pH of the solution is from 8.5 to 9.5, preferably more than 9.

3

The content of the adhesive is normally about 70 to 90 wt-% of the dry matter of the surface sizing agent. The adhesive comprises a polyvinyl alcohol and an acrylic alkylene copolymer and/or its derivatives. The content of the polyvinyl alcohol may be 30 to 40 wt-% of the dry matter of the surface sizing agent; the content of the acrylic alkylene copolymer may be 20 to 70 wt-%, preferably 20 to 50 wt-% of the dry matter of the surface sizing agent. Furthermore, the surface sizing agent may contain various additives, such as thickening agents. As an additive, it is possible to use, for example, carboxyl methyl cellulose (CMC), which improves water retention. The content of the additives is 0 to 2 wt-%, preferably not more than 1 wt-% of the dry matter of the surface sizing agent.

The inorganic agent may be an inorganic pigment known as such from papermaking, for example kaoline or talc. Mixtures of various inorganic pigments are also feasible. The content of the inorganic pigment as dry matter in the surface sizing agent is 20 to 70 wt-%, normally 20 to 30 wt-%.

The surface sizing is preferably performed with a film size press, and the surface sizing agent is then dried. After the surface sizing agent has been applied onto the surface of the base paper, the surface sizing agent may need to be neutralized to make the pH of the paper surface favourable for the subsequent silicon treatment. The surface sizing agent is neutralized to the level of pH 7 by using a suitable pH lowering agent. Thus, the water-soluble salt of the acrylic alkylene copolymer is changed, at least partly, back to a water-insoluble form.

In the following, the invention will be described with reference to the examples and the figure. The figure shows graphically the transverse expansion / water intake of a paper which has been surface sized by the formulation according to Example 1, and reference samples of prior art. The results in the figure show that the paper according to the invention expands less than the reference samples.

30

5

10

4

Example 1.

5

10

A glazing-type base paper was surface sized by using, as the surface sizing agent, a composition containing 34.5 % of polyvinyl alcohol, 34.5 % of acrylic ethylene copolymer, 30 % of kaoline, and 1 % of carboxymethyl cellulose, calculated as weight per cent of the dry matter. The acrylic ethylene copolymer was present in a solution of sodium hydroxide mixed with 20 wt-% of acrylic ethylene copolymer. In the sodium hydroxide solution, the acrylic ethylene copolymer is changed into a water-soluble sodium salt. The content of ethylene in the copolymer was 80 wt-%. The pH value of the solution was approximately 9.

The surface-sized and dried paper according to the invention was analyzed for its properties, and the results were compared with a paper of prior art. The results are shown in Table 1.

Table 1. Test results of the surface-sized paper.

Property	Measured	Unit	Paper	Paper of prior
•			according to	art
			the invention	
Thickness	average	μm	56,2	57,0
	standard	11	1,2	1,3
	deviation			
Porosity (Bekk)		S	464	158
Oil absorption (Unger	surface	g/m²	0,69	0,70
60 s)				
Shirlastain 60 s 50 %	surface	g/m²	15,9	19,0
	back	**		25,9
Cobb 60 s	surface	g/m²	13	17,3
Bekk smoothness	surface	S	3564	1266
	back	S	265	808
Gloss (Hunter 75°)	surface	%	57,6	59,5
, ,	back	%	36,8	48,7
PPS-10 roughness	surface	μm	1,3	not measured
	back	μm	2,7	not measured

5

The values given in the table were measured according to the following standards:

Thickness SCAN-P 7:75

5 Bekk porosity ISO 5627
Oil absorption (Unger) SCAN-P 37:77

as Cobb, but with Shirlastain liquid

Cobb ISO 535 10 Bekk smoothness DIN 53107

Shirlastain

Gloss TAPPI T480 OS-78 Roughness (PPS) SCAN-P 76:95

The results show that the Cobb value, which indicates the hydrophobicity of the paper, is clearly lower for the paper according to the invention than for the paper of prior art. From the Cobb values, it can be stated that values exceeding 17 g/m² are common at present, and values which are not higher than g/m² are good. For the paper of the invention, the Cobb value is typically not higher than 17 g/m², advantageously not higher than 16 g/m², and preferably not higher than 15 g/m².

Furthermore, the results show that the Shirlastain value for the surface-sized side is lower than 18 g/m². When the Shirlastain value is not higher than 18 g/m², the value is considered good.

The above description does not restrict the invention, but the invention may vary within the scope of the claims.

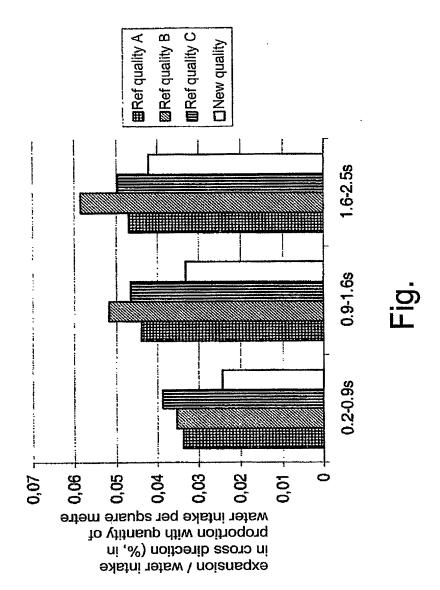
6

Claims:

5

10

- 1. A paper comprising a base paper and, on at least one side of the base paper, a surface sizing layer which contains inorganic pigment and polyvinyl alcohol (PVA), **characterized** in that the surface sizing layer comprises an acrylic alkylene copolymer and/or its derivatives.
- 2. The paper according to claim 1, **characterized** in that the comonomer of the acrylic alkylene copolymer is ethylene.
- 3. The paper according to claim 1 or 2, **characterized** in that the inorganic filler is kaoline, talc, or a mixture of these.
- The paper according to any of the preceding claims, characterized
 in that the surface sizing layer comprises carboxymethyl cellulose (CMC).



INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2004/000329

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21H 17/34, D21H 19/56, D21H 21/16, D21H 27/06 // D21H 17/36, D21H 17/37 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

C. DOCU	MENTS CONSIDERED TO BE RELEVANT			
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Х	US 3674896 A (CHESTER L. PURCELL ET AL), 4 July 1972 (04.07.1972), column 2, line 6 - line 49; column 3, line 68 - line 71; column 11, line 52 - column 12, line 69, claims 1-3	1-3		
Y		4		
				
X	WO 0117774 A1 (TETRA LAVAL HOLDINGS & FINANCE S A), 15 March 2001 (15.03.2001), page 5, line 31 - page 6, line 12, claims 1-10 	1-3		
	-			

Special categories of cited documents:		"T" later document published after the international filing date of date and not in conflict with the application but cited to und				
"A" document defining the general state to be of particular relevance	ate of the art which is not considered	the principle or theory underlying the invention				
"E" earlier application or patent but published on or after the international filing date		"X"	considered novel or cannot be considered to involve an inventive step when the document is taken alone			
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)						
		"Y"	document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is			
"O" document referring to an oral dis means	closure, use, exhibition or other		considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art			
"P" document published prior to the international filing date but later than the priority date claimed		″& <u>"</u>				
Date of the actual completion	of the international search	Date	of mailing of the international search report			
11 October 2004			1 4 -10- 2004			
Name and mailing address of the ISA/		Authorized officer				
Swedish Patent Office						
Box 5055, S-102 42 STOCKHOLM		Barbro Nilsson/Els				
Facsimile No. +46 8 666 02 86			Telephone No. +46 8 782 25 00			
Form DCTE ITC A /210 (ground shoot)	/Inner 2004)					

See patent family annex.

Further documents are listed in the continuation of Box C.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2004/000329

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	WO 0155507 A1 (UPM-KYMMENE CORPORATION), 2 August 2001 (02.08.2001), page 2, line 13 - line 32, claims 1-15	1-3
Y	· 	4
A	EP 1279768 A2 (RICOH COMPANY, LTD.), 29 January 2003 (29.01.2003), claims 1-8	1-4
Α.	US 6426120 B1 (ROBERT STOCQ ET AL), 30 July 2002 (30.07.2002), column 2, line 8 - column 3, line 5,	14
	abstract 	
Α ,	US 5807781 A (BERND REINHARDT ET AL), 15 Sept 1998 (15.09.1998), claims 1-4	1-4
,		

INTERNATIONAL SEARCH REPORT

Information on patent family members

03/09/2004

International application No. PCT/FI 2004/000329

US	3674896	A	04/07/1972	AT AU BE BR CH CH CH FI FR	6791547 208368 485827 520226 1646160 53334 1532958	B A D D A A A B,C	10/02/1972 17/04/1974 19/11/1970 29/01/1968 00/00/0000 15/11/1971 15/02/1970 15/03/1972 08/07/1971 30/12/1977 12/07/1968
				GB NL	1201811 6710476		12/08/1970 29/01/1968
WO	0117774	A1	15/03/2001	AU BR CN EP JP SE SE	7326300 0013797 1387479 1237721 2003508274 516918 9903176	A T A T	10/04/2001 14/05/2002 25/12/2002 11/09/2002 04/03/2003 19/03/2002 08/03/2001
WO	0155507	A1	02/08/2001	FI	20000151	A,V	27/07/2001
EP	1279768	A2	29/01/2003	JP US US	2003147696 6670010 20030031820	В	21/05/2003 30/12/2003 13/02/2003
US	6426120	B1	30/07/2002	AU BE EP WO	5798700 1013060 1119660 0104418	A A	30/01/2001 07/08/2001 01/08/2001 18/01/2001
US	5807781	A	15/09/1998	DE EP FI JP JP	4425737 0697484 953486 2683718 8188992	A A B	01/02/1996 21/02/1996 22/01/1996 03/12/1997 23/07/1996